Studies on Catechol-functionalized Cyclosiloxane Polymers for Hybrid Nanocoating on Flexible Substrates

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論文内容要約

Chapter I　Introduction

The assemble techniques of semiconducting nanomaterials are important in preparing well performed optoelectronic devices because the preparation procedures are mostly based on sequential deposition of different materials. Among those bottom-up approaches, layer by layer (LbL) method is of great interest in manufacturing electronic devices, because of its strong capability in assembling thin films of different materials into one system and exerting nanometer control over film thickness. Layer materials, thin film coating methods and coated substrates are three most important factors of LbL method and cooperatively affect physicochemical properties of the assembled thin films such as the thickness, homogeneity and inter and inter layer film organization. In this thesis, a layer material used for LbL method, catechol-functionalized polysiloxane (CFPS), specifically designed for nanoparticle based flexible devices was synthesized in Chapter II. The molecular structure of CFPS (Fig. 1) was inspired by a glue protein secreted by marine mussel that bond strongly to almost all organic and inorganic surfaces. The layer material is able to serve as a multifunctional platform for flexible devices because it contains the following features: 1) It induces a controllable self-assembled behavior of nanoparticles, thus manipulates device properties. 2) It will generate admirable surface robustness for a long-term durability of flexible

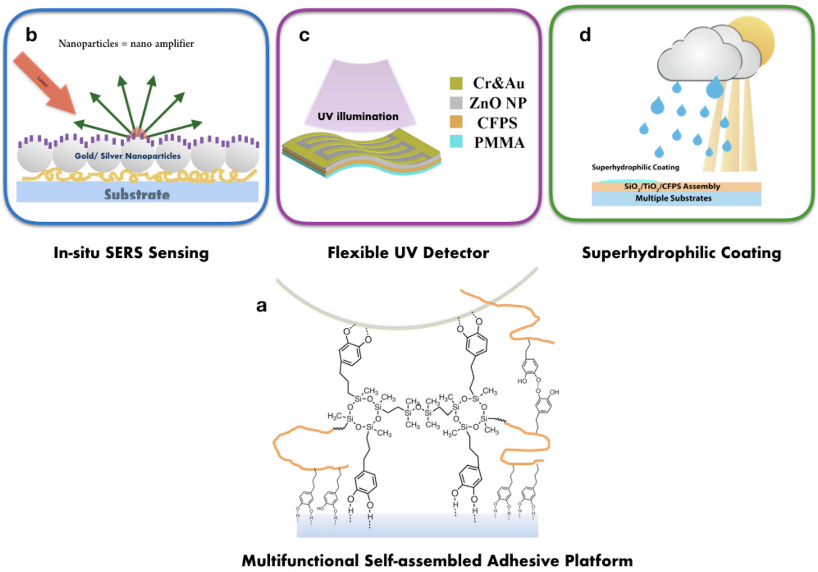

Fig.1　Catechol-functionalized polysiloxane (CFPS) for flexible nanoparticle-based device platforms.

devices, which is highly critical for true practice. 3) it has versatile compatibility for applications in different devices. Catechol can form energetic interactions with many kinds of substrates and transition metallic nanoparticles. The layer material CFPS was further applied for in-situ surface enhanced Raman scattering (SERS) sensing (Chapter III), for a long term durable ZnONP based flexible UV detector (Chapter IV) as well as for superhydrophilic surface modification on flexible polymer substrates (Chapter V). The functions of CFPS self-assembled platform were in detail studied and demonstrated in each application.

Chapter II Synthesis and Nanocoating Properties of Catechol-functionalized Polysiloxane

Eugenol, a catecholic derivative that is readily available in large quantities, was used as precursor for catechol functionalization. The first key point of the CFPS synthesis strategy is tris-(pentafluorophenyl)borane (TPFPB)-catalyzed silylation. The orthogonal reactivity of TPFPB allows the facile one-step transformation of eugenol into a reactive, bis-silyl protected DOPA mimic. The second key point of the CFPS synthesis strategy is the hydrosilylation. 1,3,5,7-Tetramethylcyclotetrasiloxane (TMCS) with four silicon hydrogen bonds and 1,3-divinyltetramethylsiloxane (DTMS) with two terminated vinyl groups were used as comonomers to form linear structure polysiloxane backbones (TMCS-DTMS polymers). Remaining silicon hydrogen bonds can further react with vinyl groups of silyl-protected eugenol through hydrosilylation for functionalization. This renders the synthesis procedure from polymerization to functionalization simply conducted in a one pot reaction. The fractional ratio of silyl-protected eugenol is 88.2% (Fig. 2), which indicates a very high concentration of catechol units introduced into the polymer backbone and will have benefits for the assembled materials with a strong adhesive property. After deprotected in mild acidic solution, CFPS was dissolved into toluene. A CFPS self-assembled thin film was prepared through dip-coating method. The CFPS self-assembled thin film has a smooth surface with a surface roughness of 4.6 nm and a thickness of 36 nm. It also has an outstanding

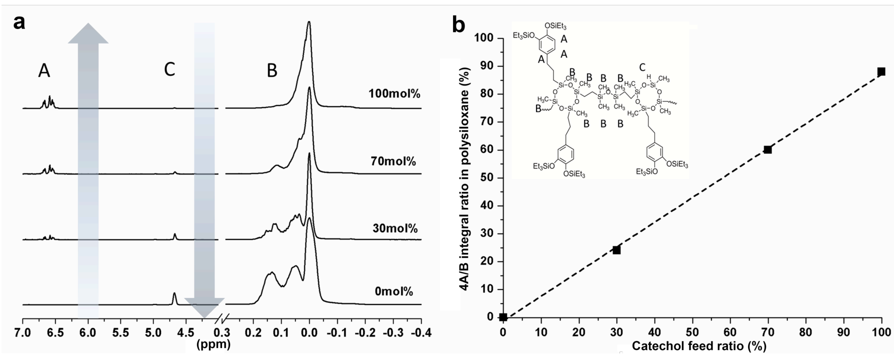

Fig. 2 Characterization of the ratio of catechol reacted with a polymer backbone. (a) ^{1}H NMR spectra of CFPS with different catechol/silicon hydrogen bond feed ratios. All spectra were normalized to the intensity of the Simethyl resonance at approximately 0 ppm. (b) Plot of the integral ratio of catechol/Si methyl (4A/B) in 1H NMR as a function of the catechol/silicon hydrogen bond feed ratio.

coating ability not only on inorganic substrates such as silica wafer, glass slide and quartz but also on flexible polymers sheets such as PMMA, PET, PEN and PI. The thin film coating was also conducted onto a PMMA substrate with a nano-grating structure.

Chapter III CFPS Self-assembled Platform for In-Situ SERS Probing

Surface enhanced Raman scattering (SERS) is a physical phenomenon based on the enhancement of the magnitude of the electromagnetic fields around a roughened silver or gold metallic surface caused by localized surface plasmon resonance. It is a powerful detection method that is able to magnify the Raman signal of chemical contamination on the skin of fruits or animals even in trace amount. In this chapter, CFPS thin film assembly was introduced into silver nanoparticle (AgNP) based SERS substrates. AgNPs are anchored onto CFPS-modified substrates using a dip coating process. Scanning electron microscopy images revealed that AgNPs were distributed homogeneously on numerous substrates. Moreover, the surface number density and average interspace of the AgNPs were tuned easily by controlling the concentration of AgNP dispersions, resulting in the tunable CFPS/AgNP SERS substrate enhancement. A substrate with high-density AgNPs exhibited excellent surface enhanced Raman scattering (SERS) performance with an enhancement factor as high as 7.89×10^7 and an ultra-low detection limitation of 0.1 nM, (Fig. 3), which can be ascribed to the ‘‘hotspots’’ formed between the adjacent AgNPs controlled by CFPS-induced self-assembly. The AgNP structures prepared on different substrates using CFPS showed a similar high intensity, suggesting a versatile platform of the CFPS film for AgNP assemblies

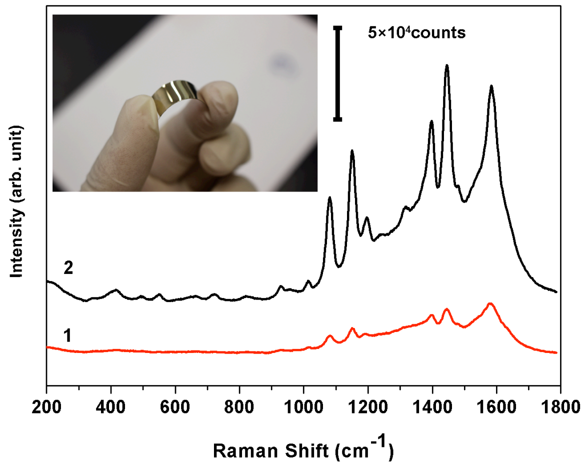

Fig. 3 SERS spectra: Line 1 and Line 2 enhancement signal using 0.1 nM and 1 mM PATP ethanol solution, respectively. (top left) PMMA-based flexible CFPS/AgNP substrate.

Chapter IV CFPS Self-assembled Platform for Flexible UV Detector

In Chapter IV, the CFPS thin film assembly was introduced into a ZnONP-based flexible UV detector to enhance the surface robustness and long-term durability of the device. The CFPS thin film assembly between flexible PMMA substrates and the semiconducting channel can strongly anchor ZnONPs through a coordination bond, thus forming an ultra-stable channel layer. A peeling test of the ZnONP channel was conducted by using a transparent 3M Scotch® tape. Laser scanned microscope proved that the semiconducting channel structure was kept integrity after the peeling test, indicating good surface robustness.

The as-prepared UV detector owns a dark and optical current of 0.35 nA and 1430 nA respectively, the on/off ratio 4.03×10^3. The properties are as good as other ZnONP-based devices prepared on the solid substrate using similar preparation methods. Finally, a bending test was conducted using a home-made bending machine. The present flexible device shows a stable UV detecting performance after one thousand times of bending at 3 mm curvature radii. The CFPS adhesive self-assembly thin film provides a promising solution to increase surface stability and long term durability for all ZnONP-based optoelectronic devices.

Chapter V CFPS Self-assembled Platform for Superhydrophilic Coating

Superhydrophlicity denotes surfaces with a water contacted angle (WCA) of less than 10°, which is an inevitable feature for applications such as self-cleaning, antifogging, anticorrosive, and pervaporation. TiO_2/SiO_2 composites coating is an effective classical method generating a UV-induced superhydrophilic surface, however problems still exist: In the preparation procedure, calcination over 500 °C is necessary to achieve good surface robustness, which impede the application of the method to polymer surfaces. In Chapter V, the CFPS adhesive thin film assembly was introduced into the procedure of hybrid nano-coating of SiO_2NP/TiO_2NP to demonstrate superhydrophlic treatment without calcination. Catechol groups can form energetic supramolecular interactions with both SiO_2NP and TiO_2NP surfaces respectively through hydrogen bonding and coordination bonding. The strong adhesion force provided by the CFPS film allows us to further extend the method into flexible electronics without calcination process. High transparency of CFPS thin film will also maintain the transparency of light at the visible light wavelengths. After the SiO_2NP/TiO_2NP deposition with CFPS, The WCA values of PMMA, aluminum, and glass slide were 3.3°, 4.5° and 4.8° respectively. Strong surface robustness was also demonstrated by a peeling test.

Chapter VI Conclusions

In the present study, the author synthesized catechol-functionalized polysiloxane (CFPS) and further used it as a platform to induce three different self-assembled hybrid thin films (CFPS/AgNP, CFPS/ZnONP, CFPS/SiO_2NP/CFPS/TiO_2NP) for different applications as SERS substrates, flexible UV detector and superhydrophilic coating. The CFPS self-assembled thin film serves as a multifunctional platform that controls the self-assembled behavior of nanoparticles and manipulates the device properties. It will provide flexible devices with strong surface robustness, which is highly critical for practice use. The diverse compatibility also renders a huge potential of CFPS adhesive in many other nanoparticle-based flexible devices.